

RESPONSE UNDER 37 C.F.R. § 1.116  
EXPEDITED PROCEDURE  
TC/A.U. 1731

### **REMARKS/ARGUMENTS**

Claims 16-45, 54, 59-61 and 63-66 are pending in this application.

Claims 1-15 and 46-53 were previously cancelled.

Claims 55-58 and 62 are cancelled by this Amendment.

New independent claims 63-66 have been added. They correspond to previously presented independent claims 16, 30, 38 and 59 as set forth in the last Amendment, but with the incorporation of the allowable subject matter of previously presented dependent claim 56 (the epoxy-reactive polymer is a carboxylated vinyl acetate-ethylene terpolymer emulsion). Therefore these new claims should be allowable.

Similarly, independent claims 16, 30, 38, 54 and 59 have been amended to also incorporate the allowable subject matter of previously presented claim 56, which is hereby cancelled. In addition, these independent claims have been further amended to delete the recitation inserted in the previous Amendment that the epoxy-functional polymer contains 10 or more pendant epoxy moieties. However, it is believed that recitation is unnecessary to distinguish over the cited prior art in view of the insertion of the allowable subject matter specifying that the epoxy-reactive polymer is a carboxylated vinyl acetate-ethylene terpolymer emulsion. Therefore all of the remaining claims are believed to be patentable over the cited prior art of record.

With regard to the outstanding double patenting rejections, claims 16-37 stand provisionally rejected under 35 U.S.C. 101 as claiming the same invention as that of claims 22-35, 42 and 48-54 of co-pending Application No. 10/893,209. However, in light of the foregoing amendments to all of the independent claims in this application and recent amendments to co-pending Application No. 10/893,209, the basis for this rejection has been overcome.

Claims 38-45 stand provisionally rejected on the ground of non-statutory obviousness-type double patenting as being unpatentable over claims 55-62 of co-pending Application No. 10/893,209. To meet this objection, a terminal disclaimer is submitted herewith.

Claims 16-32 and 30-45 stand provisionally rejected on the ground of non-statutory obviousness-type double patenting as being unpatentable over claims 12 and 21-46 of co-pending Application Serial No. 10/893,094. The provisional rejection is based in part on the assertion that the "azetidinium-functional polymers are epoxy-functional polymers". However, this is not correct. More specifically, azetidinium resins are based on the reaction of secondary amines with epichlorohydrin (epichlorohydrin is the most common reactant used) to form a tertiary amine which will form a ring to quaternize the nitrogen: an azetidinium ring. Although formed from a reagent that contains an epoxy-functional group (epichlorohydrin), the polymer no longer contains an epoxide ring, but instead an azetidinium ring. On the other hand, epoxide resins are based on the reaction of tertiary amines with

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epihalohydrin (i.e., epichlorohydrin) to result in the direct quaternization of the nitrogen and the addition of the epoxide ring to the molecule. These resins have an epoxide functional group and are unstable in this form (very reactive). The resins are acidified with hydrochloric acid to form the more stable chlorohydrin form. The resin can be converted back to the reactive epoxy form with a base.

The differences between azetidinium resins and epoxide resins are further illustrated in the attached pages 16-17 and 20-21 of the text "Wet Strength Resins and Their Applications", which was incorporated by reference at page 4 of Applicants' specification. Based on the foregoing explanation, it is believed that the differences between the claims of this application and the those of the cited co-pending application are not obvious and that a terminal disclaimer is not appropriate.

It is therefore believed that this application is now in condition for allowance and such action is earnestly solicited.

Please charge any prosecutorial fees which are due to Kimberly-Clark Worldwide, Inc. deposit account number 11-0875.

The undersigned may be reached at: (920) 721-3616.

Respectfully submitted,  
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#### CERTIFICATE OF TRANSMISSION

I, Judy Garot, hereby certify that on June 26, 2006 this Amendment and a five-page attachment are being facsimile transmitted to the United States Patent and Trademark Office, Fax No. (571) 273-8300.

Typed or printed name of person signing this certificate:

\_\_\_\_\_  
Judy Garot

Signature:

\_\_\_\_\_  
Judy Garot

# **Wet-Strength Resins and Their Application**

*A project of the Papermaking Additives  
Committee of TAPPI's Paper and Board  
Manufacture Division*

**Committee Assignment No. 810506.03**

**Lock L. Chan, Task Group Chairman and Editor**

**TAPPI**

## Wet-Strength Resins and Their Application

resins are derived from secondary aminopolyamides, the 3-hydroxyazetidinium ring is likewise their principal reactive functional group (9, 10), and they may be referred to as "azetidinium" resins.

Tertiary amines react with epi by initial opening, then reclosure of the epoxide ring with expulsion of chloride ion, to form a glycidyl (2,3-epoxypropyl) ammonium salt. Resins based on the tertiary amine-epichlorohydrin reaction will be called "epoxide" resins. This term refers to the functionality of the resin, not to the epoxide group of the epichlorohydrin precursor of both classes of resins.\*

These functional groups can occur independently of the category of backbone polymer. Thus, resins with either azetidinium and epoxide functionality have been based on backbone poly(aminoamides), depending on the kind of starting amine groups. The commercially significant azetidinium resins are principally of the PAE (polyamide) and PAPAE (polyalkylene-polyamine) type. Currently important epoxide resins are of the PAE and the APE (amine polymer) type.

The section on resin chemistry is organized according to the type of polymer backbone. However, the qualitative differences in handling, performance, and reactivity of the resins in paper depend more on the differences between azetidinium and epoxide resins than on differences among backbone polymers. Therefore, some of the discussion of applications technology is organized around the functional groups.

## Classes of Polymeric Amine-epichlorohydrin Resins

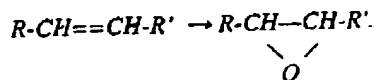
### Polyamides and Other Condensation Polymers

#### Secondary amine-based azetidinium resins

##### Saturated and aromatic acids

In the original patents (1, 2) for wet-strength resins of this class, the polyamides were based on saturated aliphatic dicarboxylic acids and polyalkylenepolyamines containing two primary amine groups and at least one secondary amine group. An example is the first commercial resin, derived from adipic acid and diethylenetriamine (DETA) (Figure 2.2).

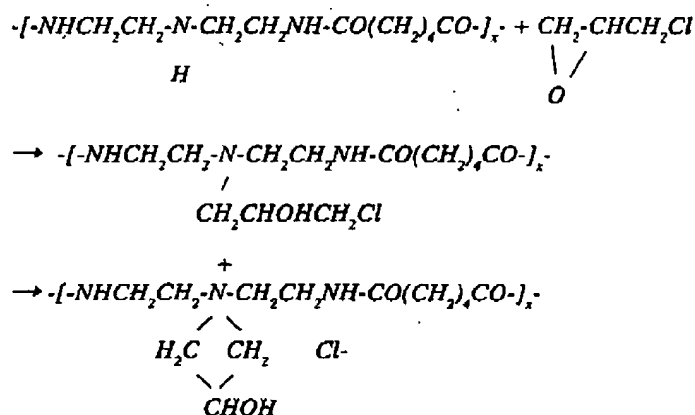
\*In this connection, it may be mentioned that the term "epoxidation" customarily refers to the conversion of a double bond to an epoxide,



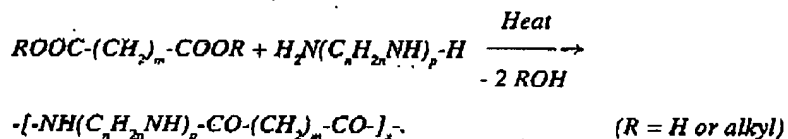
The attachment of a glycidyl group to an amine,

## Alkaline-Curing Polymeric Amine-Epichlorohydrin Resins

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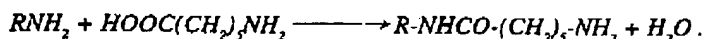
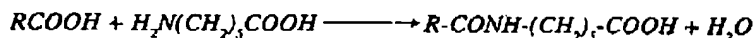
**Figure 2.2. Formation of Adipic Acid-DETA Polyamide-epichlorohydrin Resins**

In most known commercial PAE resins, the acid moiety ( $C_6$  or below for reasons of solubility) is derived either from the dicarboxylic acids themselves (1, 2) or their esters (11):



The patent literature also describes analogous resins based on higher aliphatic diacids (12-15), fatty (mono)acids (16), alicyclic (17, 18), and aromatic acids (19-24), as well as aliphatic acids containing heteroatoms such as oxygen (1) or nitrogen (25-29).

Caprolactam and 6-aminocaproic acid are components of some polyamide wet-strength resins (30-39) and dewatering aids (40). They will react with either a carboxyl or an amine end group to form an amide group and regenerate a similar end group:



Copolymerization with aminocaproic acid can introduce amide-containing "spacer" units without introducing more amine sites for attaching epichlorohydrin. Aminobutyric acid and its corresponding five-membered cyclic lactam have also been described as polyamide resin components (41). Caprolactam is also used alone (42) or as the precursor of complex dibasic acids (36, 37, 43, 44) in other wet-strength resins and processing aids. Lactones (cyclic esters) have been described as coreactants with acids and polyamines in the formation of polyamide-polyester resins (45-47).

pentaethylenhexamine (PEHA). Mixtures of two or more polyamines are also disclosed (24, 75), as is the partial replacement of a polyamine by a diamine (1, 2). Historically, the principal polyamine component of polyamide resins has been diethylenetriamine (DETA). In the United States, at least, the PAE resins of greatest commercial importance are those based on DETA, since Food and Drug Administration clearances for their use in food packaging describe only DETA-based resins (76).

The patent literature describes the partial replacement of the polyamine component by diamines (1, 2), alkanolamines (77, 78), and polyglycols (79) to yield copolyamide or polyester-polyamide resin precursors. Mixtures of separate polyalkylenepolyamines and polyalkylenepolyamine-dibasic acid polyamides have been coreacted with epichlorohydrin (80-84). In most, the separate polyamine has been a polyethylenepolyamine, although methylbis(aminopropyl)amine has been used (84).

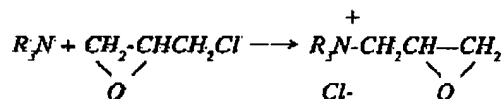
Basic nitrogen compounds such as ethylenediamine, added with resin to the pulp, have been described as curing accelerators for PAE and PAPAE resins (85).

#### Modified poly(aminoamide)-epichlorohydrin resins

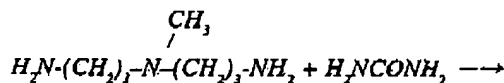
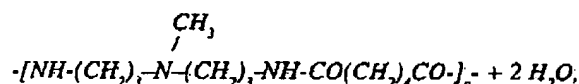
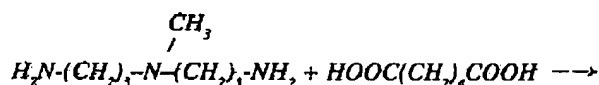
At least experimentally, polyaminoamide precursors have been modified before the epichlorohydrin reaction (Figure 2.11), by treatment with dicyandiamide or guanidine hydrochloride (86), acrylonitrile (87), acrylamide (88, 89), ethylene oxide (90, 91), formaldehyde (92), or sodium chloroacetate (35).

#### Tertiary amine-based epoxide resins

In these resins, a tertiary amine reacts with the epoxide of epichlorohydrin to form a glycidyl quaternary ammonium salt:



The first condensation polymers to employ this chemistry were based on methylbis(3-aminopropyl)amine ("MBAPA," also known as methyliminobispropylamine), which was condensed by heating with urea to give a polyureylene (or thiourea to give a polythioureylene) (93), with dicarboxylic acids or esters to form polyamides (94-96) or copolyamides (97-99), or with both to give polyamide-polyureylenes (100, 101) (Figure 2.7).



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## Alkaline-Curing Polymeric Amine-Epichlorohydrin Resins

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The glycidyl quaternary ammonium resins ("epoxide" resins) are characterized by high efficiency and high off-machine wet strength. As a class, they can impart more wet-strength than azetidinium resins after oven-curing, and they can develop a higher proportion of their ultimate wet-strength during the drying operation.

If left in the epoxide form as made, these resins can lose their effectiveness because the epoxide group is hydrolyzed much faster than the azetidinium group. However, their reaction with hydrochloric acid converts the epoxide groups to chlorohydrin groups (102). In the chlorohydrin form, the resins are stable in concentrated solution for a long time without loss of potential effectiveness. They are reactivated just before use, by treatment in dilute solution with enough alkali to reconvert the chlorohydrin to the epoxide form (102). The stabilization and reactivation are discussed in more detail below.

**Polyamine (Polyalkylenepolyamine) Resins**

A few amine-epichlorohydrin resins have been described, based on ammonia (103, 104) or methylamine or similar amines (104), alone or in combination with polyamines (105). However, polyamine-based resins have been investigated much more extensively. With a few exceptions, the polyamines are based on C<sub>2</sub>, C<sub>3</sub>, or C<sub>6</sub> alkylene units, of which the last are of the most commercial importance.

**Polyethylenepolyamines (poly-C<sub>2</sub>-polyamines)**

Polyethylenepolyamine-based resins, e.g., triethylenetetramine- and tetraethylenepentamine-epichlorohydrin, were among the first to be patented (106). Other examples are based on polyethylenimine (PEI) (107, 108), or (for use in dewatering) polyethylenepolyamine still bottoms (pentamines and higher) (109). PEI crosslinked with vinylcyclohexene dioxide has also been described (110). From a study of the kinetics of the reaction of epichlorohydrin with ethylenediamine, DETA, and PEI, it has been concluded that PEI for wet-strength applications should be as linear as possible (111). Resins of this class have not become important commercially in wet-strength applications because of their modest cost effectiveness.

A number of resins have been described in which a polyalkylenepolyamine is chain-linked to a polymer before the crosslinking reaction with epichlorohydrin. These are more numerous among resins based on C<sub>3</sub> and higher alkyleneamines. However, polyethylenepolyamine-diglycidyl ether precondensates, such as TETA linked with the diglycidyl ether of 4,4'-isopropylidene-bisphenol, have been described as precursors of epichlorohydrin wet-strength resins (112).

1,2-Dichloroethane-linked prepolymers from tetraethylenepentamine (TEPA) or from TEPA-adipic polyamide are nonthermosetting resins that (in combination with other polymers) increase dry strength without imparting wet strength (113).

**Poly(trimethylene)polyamines (poly-C<sub>3</sub>-polyamines)**

Bis(3-aminopropyl)amine (also known as iminobispropylamine or IBPA), H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, has been reacted with epichlorohydrin to make wet-strength resins, both alone (114), and as an extended prepolymer made by chain-linking with 1,2-dichloroethane (115). Poly-C<sub>3</sub> (and higher) polyamine-epi products have also been described as auxiliaries such as flocculants (116).

N-alkyl-1,3-propanediamines have been reacted with epichlorohydrin, directly to make paper sizing compositions (117), or with DETA-epichlorohydrin and TEPA-epichlorohydrin